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REFRACTORY MATERIALS RESISTANT TO THE ACTION
OF FLUORIDES AND ANHYDROUS HYDROFLUORIC ACID

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Modern chemical technology employs some processes and equipment in which metal fluorides or hydrogen fluoride come in contact with a refractory lining at high temperatures, e.g., in the processing of apatite-nephelinic rocks, obtaining aluminum fluoride and others. It is known also that the fluoride most used in industry, fluorspar (CaF_2), is widely utilized in metallurgy, and the silicate and chemical industries. In all these cases it is necessary to have refractory materials able to withstand the action of fluorides.

The purpose of this work is to select lining materials for furnaces in which fluorides are melted, and also for rotary and shaft furnaces in the atmosphere of which hydrogen fluoride and steam are present.

Since complete reproduction of complex industrial processes is impossible under laboratory conditions, it has been necessary, in addition to modeling the furnace to divide the processes into separate parts. Altogether, three methods have been employed for conducting experiments.

1. Testing the refractory materials according to the crucible method by melting fluorspar or its mixture with nepheline.
2. Testing with the same materials in the melting bath under action of water vapor.
3. Testing the refractory materials in an atmosphere of hydrogen fluoride mixed with water vapor in a tube furnace model.

Fifteen various refractory materials were tested at high temperatures.

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Crucible Method

Testing was conducted in the following way. A hole of 60 mm diameter and 35 mm depth was drilled in the sample of the refractory already made; or during the forming of the sample a cylindrical depression was made, 30 mm in diameter and 30 mm in depth. The hole in the refractory material was filled with a weighed sample of the reaction mixture and all samples were heated in the furnace according to an established curve. On cooling, the samples were sawed crosswise, polished, and the area of corrosion and impregnation was measured.

To clarify the process of deterioration in refractory materials, the chemical composition of the boundary layer between the refractory and melt was studied for the chamotte and high-alumina refractories. In addition thin sections were cut out of the walls of the crucibles and examined under a microscope.

Chamotte and corundum-andalusite refractories are unsuitable under conditions involving action by a fluorspar melt, which quickly dissolves them. The boundary layer deteriorates in the case of silica and alumina and is enriched with lime contained in the newly formed anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Fluorine traces are observed in the boundary layer, which factor is probably due to the rapid removal of all formed fluorides at the temperature of the experiment.

Dolomitic and clinker-concrete refractories are very porous, absorb fluorspar and, although not corroded by it, are also unsuitable for lining because of cracking and hydration.

Carbonaceous refractory does not change under the action of fluorspar, but its use is impossible for lining a flame furnace, in the atmosphere of which oxygen is present.

The best resistance was evidenced by fused magnesite and chrome-magnesite 2; however, the entire melt was absorbed by the crucible walls.

Sintered magnesite was noticeably corroded and saturated with the melt.

Testing in Melting Bath

A model of the melting bath was constructed on the bottom of an oil laboratory furnace. It was made of 230 x 113 x 65 mm bricks which had been weighed and numbered. A porcelain pipe of 10-15 mm in diameter was led into the furnace through the roof to a point 20-30 mm from the bath bottom. Water vapor was delivered through this pipe under pressure of 1.3-1.5 atm after the reaction mixture had been melted. Upon completion of the experiment and cooling of the furnace, the melting bath was taken apart and the bricks were weighed and examined. The lining of the bath could be made from the several types of refractories under investigation, thus, facilitating comparison of the fluoride resistant properties of these materials.

All bricks were joined with a mixture of magnesite or chrome-magnesite powder (grain smaller than 0.5 mm) in sulfite-cellulose extract (3 percent). No corrosion of joints was observed in any case. It has been found that the best mortar for brick work consists of 75 percent sintered magnesite powder and 25 percent chromite.

Experiments were conducted under the following conditions:

Series One (4 experiments). Temperature 1500 degrees; charge-fluorspar (97 percent CaF_2); length of each experiment-4 hours.

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Series Two (3 experiments). Temperature 1150-1200 degrees; charge-54 percent fluorspar and 46 percent nepheline; length of experiments-2-4 hours. Steam only slightly decomposed fluorspar because the porcelain pipe was quickly dissolved in the melt.

Bricks of fused and sintered magnesite had a slightly washed out surface but fracture showed sound material. Evidently, their corrosion proceeded slowly and uniformly.

The surface of chrome-magnesite brick became spongy, some grains were crumbled out, probably, because of partial deterioration of the chromite grains and binding agent.

The corundum-chamotte refractory exhibited a spongy structure after the experiment. The chamotte component was greatly washed out. The multichamotte brick was quickly corroded with fluorspar and evidently is not suitable for the bath lining.

Fused mullite, because of its high degree of hardness, was tested in the form of fragments submerged in melts of fluorspar and fluorspar-nepheline mixture. Pieces of fused mullite were slightly corroded on the surface and covered with a crust composed of yellow-brown and red grains of corundum. The strength of samples was not lowered and the melt did not penetrate. Evidently, the corundum crust prevents further destruction of the refractory.

Testing in the Pipe Furnace

Ten series of experiments 2-4 hours in length were conducted in a pipe furnace at temperatures from 500 to 1400 degrees. Two platinum boats were loaded with three types of refractories (2 samples of each) for every experiment. In addition, six types of refractories were tested in a gas mixture (15% HF+15% H₂O) for 12 hours at 1400 degrees. Fragments of 2-3 grams were used as refractory samples.

Many of them were examined microscopically and the chemical composition of some samples was determined before and after treating them in the gas mixture.

The majority of refractory materials are comparatively quickly deteriorated at high temperatures under the action of hydrogen fluoride or its mixture with water vapor, and especially under action of melts containing fluorine. Their structure is disrupted and their chemical composition is modified due to the elimination of those components which form compounds with fluorine volatile at high temperatures. Such elements are: silicon, iron, titanium, alkaline metals and, probably, chromium. Greater stability in refractory materials is revealed by the alkali earth metals and aluminum (mainly in the form of crystalline corundum).

In addition to the influence of the chemical nature of refractories on their resistance to fluorine-containing gases and melts, the compactness of refractories also plays an essential role in this relation. The action of calcium fluoride in pure state at 1500 degrees is considerably stronger than that of its mixture with nepheline at a temperature of 1200 degrees. The action of air mixed with hydrogen fluoride and water vapor increases in intensity with an increase in the mixture's concentration and the reaction temperature. The intensity of the corrosive process in cases of fluorspar-containing melts is not conditioned by fluorine alone but also depends on the calcium oxide formed in the reaction, which usually shows a very high activity toward acid oxides at high temperatures. The best resistance to fluorides was revealed by magnesite brick and fused mullite.

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Definite qualitative data under conditions of action by the $\text{HF} + \text{H}_2\text{O}$ mixture were not obtained, and therefore comparative evaluation of the resistance ability of refractories is difficult in this case. However, fused mulite and magnesite refractories may be considered as the most stable materials. Satisfactory resistance was also demonstrated by high-silica and multichamotte refractories.

New formations were detected in magnesite refractories, but their nature and properties are not sufficiently clarified as yet. These formations are subject to further investigation to determine their composition and role in the protection of refractory surfaces against corrosion by hydrogen fluoride.

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